ELECTRODES FOR SOLID STATE GAS SENSOR

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Related U.S. Application Data

Continuation of application No. 09/770,359, filed on Jan. 25, 2001, now abandoned.

References Cited

U.S. PATENT DOCUMENTS
3,216,911 A 11/1965 Kronenberg et al. .......... 204/1
3,576,730 A 4/1971 Spacil ......................... 204/195
4,177,125 A 12/1979 Barnabe .................... 204/195
4,220,517 A 9/1980 Niwa et al. ................ 204/195
4,277,323 A 7/1981 Muller et al. ............... 204/195
4,304,651 A 12/1981 Wakahisa et al. ........... 204/195

4,462,891 A 7/1984 Lawless ..................... 204/427
4,786,374 A 11/1988 Worrell et al. ............. 204/1
5,173,166 A 12/1992 Tomantscgher et al. .... 204/412
5,958,214 A 9/1999 Nikolskaja .................. 205/784

OTHER PUBLICATIONS


(List continued on next page.)

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ABSTRACT

A mixed potential electrochemical sensor for the detection of gases has a ceria-based electrolyte with a surface for exposing to the gases to be detected, and with a reference wire electrode and a sensing wire electrode extending through the surface and fixed within the electrolyte as the electrolyte is compressed and sintered. The electrochemical sensor is formed by placing a wire reference electrode and a wire sensing electrode in a die, where each electrode has a first compressed planar section and a second section depending from the first section with the second section of each electrode extending axially within the die. The die is filled with an oxide-electrolyte powder and the powder is pressed within the die with the wire electrodes. The wire-electrodes and the pressed oxide-electrolyte powder are sintered to form a ceramic electrolyte base with a reference wire electrode and a sensing wire electrode depending therefrom.

6 Claims, 2 Drawing Sheets
OTHER PUBLICATIONS


* cited by examiner
Fig 3

Fig 4
ELECTRODES FOR SOLID STATE GAS SENSOR

RELATED APPLICATIONS
This application is a continuation of U.S. patent application Ser. No. 9/770,359, filed Jan. 25, 2001 now abandoned.

STATEMENT REGARDING FEDERAL RIGHTS
This invention was made with government support under Contract No. W7405-ENG-36 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION
The present invention relates generally to solid state gas sensors, and, more particularly, to mixed-potential sensors based on oxygen-ion conducting electrolytes.

BACKGROUND OF THE INVENTION
Mixed potential gas sensors are currently being developed for combustion control and environmental monitoring applications. The devices typically are comprised of two different catalytic electrodes deposited on a solid electrolyte. Multiple reduction-oxidation reactions occurring between the gas-phase and the electrodes cause mixed potentials of differing magnitude to develop at the dissimilar electrodes. The differences in heterogeneous kinetics, electrokinetics and the equilibrium potentials for these reactions all influence the device response to varying concentrations of analyte gas.

An example of a mixed potential device is a carbon monoxide sensor consisting of a porous platinum electrode and a porous gold electrode deposited on a zirconia based oxide electrolyte. The following electrochemical reactions occur on both the gold and platinum triple phase interfaces at differing rates:

\[ \text{O}_2 + 4e^- \rightarrow 2\text{O}^- \]
\[ \text{CO} + \text{O}^- \rightarrow \text{CO}_2 + 2e^- \]

Mixed-potential sensors based on oxygen-ion conducting electrolytes have been studied by D. E. Williams et. al. demonstrated the working of a “Pt/YSZ/Au” CO-sensor operating at T ≤ 400°C. Since that time several metal and metal-oxide electrodes have been used to design various mixed-potential sensors for the detection of CO, NO, and hydrocarbons. Although all these sensors do give a response in the presence of reducing-gases, their lack of stability, reproducibility and selectivity have hindered the commercial development of sensors based on this technology.

Various objects, advantages and novel features of the invention will be set forth in part in the description which follows, and, in part, will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

SUMMARY OF THE INVENTION
The present invention includes a mixed potential electrochemical sensor for the detection of gases. A ceria-based electrolyte is formed with a surface for exposing to the gases to be detected, and with a reference wire electrode and a sensing wire electrode extending through the surface of the electrolyte and fixed within the electrolyte as the electrolyte is compressed and sintered.

The electrochemical sensor is formed by placing a wire reference electrode and a wire sensing electrode in a die, where each electrode has a first compressed planar section and a second section depending from the first section with the second section of each electrode extending axially within the die. The die is filled with an oxide-electrolyte powder and the the powder is pressed within the die with the wire electrodes. The wire-electrodes and the pressed oxide-electrolyte powder are sintered to form a ceramic electrolyte base with a reference wire electrode and a sensing wire electrode depending therefrom.

BRIEF DESCRIPTION OF THE DRAWINGS
The accompanying drawings, which are incorporated in and form a part of the specification, illustrate embodiments of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

FIG. 1 is a cross-sectional view of a sensor according to one embodiment of the present invention.

FIGS. 2A and 2B are side and top views showing an exemplary die for forming the sensor shown in FIG. 1.

FIG. 3 graphically demonstrates the response to various gas mixtures of a variety of sensors formed in accordance with the present invention.

FIG. 4 graphically illustrates the stability of sensor #5 shown in FIG. 3.

DETAILED DESCRIPTION
This invention is a mixed-potential electrochemical sensor for the detection of gases, such as CO, NO, and non-methane hydrocarbons, in room air. The sensor utilizes a ceria-based electrolyte, and metal wire electrodes. The stability and reproducibility of the sensor is achieved by using wire electrodes instead of the usual thin or thick film electrodes that are currently employed. The metal wire-electrodes are directly embedded into the electrolyte and co-sintered in order to produce a stable metal/electrolyte interface. A suitable ceria-based electrolyte is Ce$_{0.9}$Gd$_{0.1}$O$_{2-x/2}$, where 0 ≤ x ≤ 0.25 and A is selected from Y, Sc, or Lanthaneide.

The selectivity of the device is achieved by the proper selection of the metal wire-electrodes used. Pt is used as a pseudo-reference electrode and the sensing electrode can be selected form a wide variety of metals or alloys, based on the gas that is to be sensed. For example, a Au wire is used to sense CO in room air; other precious metal wires such as Ag, Pd, or Rh can be used, depending on the gas to be detected.

The specific approach involves the following steps:
1) Embedding the metal wires in the oxide-electrolyte powder.
2) Pressing the powder along with the embedded wires in a die to form the sensor.
3) Polishing off the excess electrolyte powder in order to expose the metal wire-electrode.
4) Co-sintering the wire-electrodes along with the electrolyte powder in order to give mechanical strength and sufficient ionic-conductivity to the electrolyte.

FIG. 1 illustrates one embodiment of a sensor according to the present invention. Electrolyte body 10 is formed of Ce$_{0.9}$Gd$_{0.1}$O$_{2-x/2}$. Reference electrode 12 is formed of Pt and sensing electrode 14 is formed of Au. A Ce$_{0.9}$Gd$_{0.1}$O$_{2-x/2}$ powder (0.01–10 μm in diameter, and, preferably, 1–3 μm (Prairix)) was the starting material. The Au and Pt wires
The second improvement over existing technology is that the "burn in" period before a stable signal is achieved is much shorter than existing semiconductor sensor technology. Semiconductor sensor devices must be preheated for periods of days before stable reproducible signals are achieved. The present devices show steady signals on the initial heatup.

The configuration disclosed in this invention can be used in all types of mixed-potential sensors that utilize a solid-electrolyte and metal or alloy electrodes. A specific application is a home CO sensor for room air monitoring. The Pt-wire/CeO₂/GdO₂/O₂-Au-wire sensor has been tested for the measurement of CO in room air. This sensor with an activated carbon filter has been found to meet the sensitivity, response time, interference and stability standards stated in the UL 2034 (1995) standards. The sensor gives a 40 mV response for 100 ppm of CO with a response time <1 minute, and shows <2 mV interference for contaminants like methane, isopropanol, ethanol and heptane. The sensor has also been found to be stable for up to 2 months of continuous operation at 400°C.

The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching.

The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

What is claimed is:

1. A mixed potential electrochemical sensor for the detection of gases comprising:
   - a ceria-based electrolyte having a surface for exposing to the gases to be detected;
   - a reference wire electrode and a sensing wire electrode extending through the surface of the electrolyte and fixed within the electrolyte as the electrolyte is compressed and sintered.

2. The sensor according to claim 1 wherein the reference wire electrode is Pt.

3. The sensor according to claim 1, wherein the sensing wire electrode is Au or Rh.

4. The sensor according to claim 1, wherein the ceria-based electrolyte is Ce₁₋ₓAₓO₂₋ₓ, where 0 ≤ x ≤ 0.25 and A is selected from Y, Sc, or Lanthanide.

5. The sensor according to claim 4, wherein the reference wire electrode is Pt.

6. The sensor according to claim 4, wherein the sensing wire electrode is selected from the group consisting of Au, Ag, Pd, and Rh.

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